

**CREEP AND TEMPERATURE-DEPENDENT CREEP OF
ONE COMPONENT POLYURETHANE ADHESIVES FOR
GREEN WOOD GLUING**

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ABSTRACT

Creep and temperature-dependent creep, characteristic of one component polyurethane adhesives for wet and green structural wood gluing such as in glulam are two different parameters. Testing of the best standards-approved commercial polyurethane adhesive for this purpose shows that while ambient temperature creep is limited this is not the case for temperature-dependent creep. The commercial adhesive formulation characteristics that minimize or enhance ambient temperature and temperature-dependent creep are identified.

KEYWORDS: Adhesives; polyurethane; creep; green gluing; glulam; TMA; NMR

INTRODUCTION

Bonding of timber of high moisture content, as high as 80 % moisture content, namely “gluing wet wood”, or gluing of green wood as it is sometime called, to prepare glulam and fingerjointing became possible with the industrial introduction of honeymoon, fast-set, separate application phenol-resorcinol-formaldehyde (PRF) adhesives in the early 1980’s (Parker et al. 1990, Kreibich 1996, Vrazel and Sellers 2004, Sterley 2004). Green wood gluing became particularly interesting

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with the use of one component polyurethane adhesive systems. Their use for wet and “green” wood gluing is relatively new (Cameron and Scheepers 1985, Vick and Okkonen 1998, Radovic and Rothkopf 2003). While wet wood gluing up to 90 % moisture content of the timber was already achieved commercially in the early 1980’s (Cameron and Scheepers 1985, Radovic and Rothkopf 2003) only more recently single application, one component polyurethane systems for “gluing wet wood” have been formally approved and widely promoted for use in structural glulam in some European countries.

The main problem associated with polyurethane structures, even cross-linked ones is that of creep. Considering that the majority of the applications for glulam and fingerjointing is for structural building applications this can be a grave defect indeed. Differently from creep, temperature-dependent creep is a somewhat different effect, but critical to the safety of under-roofing structural timber in hot countries and in the behaviour of structures in fires. The concern for creep under load, and for temperature-dependant creep, is only recently starting to be addressed (Properzi et al. 2002, 2003, George et al. 2003, Richter and Schirle 2002, Na et al. 2005, Clauß et al. 2011) as a serious threat to the structural application for which some of these resins have already been approved in a few European countries.

Extensive work on the correlation of structure, creep and temperature-dependent creep for polyurethanes for structural wood application has been published (Na et al. 2005). This was done to establish basic principles in order to formulate or to reformulate the existing “creeping” formulations so that the problem can be eliminated or at least minimized. Basic principles on the structure of simple polyurethane adhesives influencing temperature-dependent creep were also identified and discussed (Na et al. 2005). The higher is the proportion of all hardened network nodes the lower is likely to be creep at ambient temperature. Instead, due to segment movement and easier disentanglement with increasing temperature, the lower is the proportion of covalently-linked nodes and the greater the proportion of just physical entanglement nodes the greater will the temperature-dependent creep be. Three of the six standard-approved polyurethane adhesives tried by other authors (Richter and Schirle 2002), namely two of the the medium-creeping ones and a bad-creeping one were tested for temperature-dependent creep, and all of them were found to be subject to extensive temperature-dependent creep. The reasons at molecular level of this effect were also determined and discussed.

This paper deals first with testing for ambient-temperature creep as well as for temperature dependent creep the two best, approved, polyurethane adhesives tested by other authors. Secondly with trying to correlate temperature-dependent creep with the structure obtained from the analysis of these two best, low-creep commercial one-component polyurethanes approved for this purpose and commercially available in the European market.

MATERIAL AND METHODS

The two best commercial polyurethane (PU) adhesives (Richter and Schirle 2002), both produced by the same source in a central european country, both approved in Germany, Sweden, France and a couple of other countries for exterior grade structural application to glulam and fingerjointing, were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Six samples of beech wood alone, and of two beech wood plys each 0.6 mm thick, after conditioning at 14 % equilibrium wood moisture content of the wood, were spread at the manufacturers recommended spread of 200 g.m⁻² with each adhesive system and then bonded at elevated temperature (100°C) and under pressure (6 kg.cm⁻²) to ensure complete

cure of the joint, and then conditioned at ambient temperature and to a constant equilibrium moisture content of 9 % to give bonded joints of 50x40x1.2 mm. These samples were then cut to dimensions of 21x6x1.2 mm for testing. Triplicate samples were then tested in isothermal mode at 40, 50 and 100°C with a Mettler 40 TMA thermomechanical analysis apparatus in three points bending on a span of 18 mm exercising a dynamic force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 seconds (6s/6s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$ allows the calculation of the Young's modulus E for each case tested, and this was done to follow the increase of modulus (MOE) as a function of temperature and time.

The liquid ^{13}C NMR spectra of the two commercial polyurethane (PUR) resins used were obtained on a Brüker DSX 400 FT-NMR spectrometer using dimethyl sulfoxide (DMSO) as solvent. Only one of them is reported in this paper. Chemical shifts were calculated relative to tetramethylsilane (TMS) at ambient temperature for NMR shifts control. However, the spectra were done at 80°C due to the high viscosity of the PUR specimens. Thus, the shifts obtained at 80°C are slightly different from those that would be expected at ambient temperature. The spectra were done at 62.90 MHz for approximately 1000 transients. All the spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

Small glulam laboratory beams of dimensions 500x25x60 mm and 500x25x30 mm (length by width by depth) of poplar wood of 450 kg.m⁻³ density were bonded with the best prestepped polyurethane wood adhesive in the temperature range 16-25°C, in the moisture content interval 15 to 65 % relative humidity. A constant force of 1500 N was applied to the first set of beams and of 500 N to the second set of smaller beams. Beech (*Fagus sylvatica* L.) wood strips of dimensions 120x25x3 mm were conditioned at 50, 30 and 15 % wood moisture content and then bonded with the polyurethane adhesive at those moisture contents. The test used was in tensile shear according to BS 1204, Part 1, with the specimens assembled to have a bonded overlap of 25x25 mm, then clamped and left in the clamp at 20°C. The shear strength and percentage wood failure increases as a function of time of a set of specimens were tested initially at 2, 4, 24 hours and 7 days after joint preparation. A number of 24 hours and 7 days specimens were also tested after 24 hours immersion in cold water and after 2 hours immersion in boiling water, both types tested wet.

RESULTS AND DISCUSSION

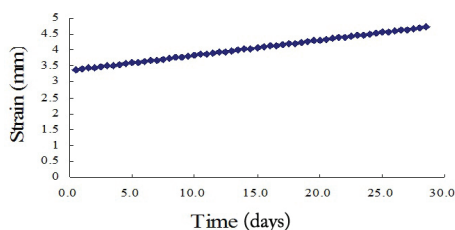


Fig. 1a

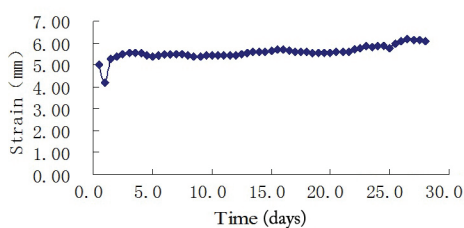


Fig. 1b

Fig. 1: Strain as a function of time (creep) over a period of 30 days laboratory glulam beams of poplar wood (450 kg.m⁻³ density), at ambient temperature (16-25°C) and air humidity 15-65 %, wood moisture content at gluing = 11 %. a) of dimension 500x25x60 mm, constant force 1500 N. b) of dimension 500x25x30 mm, constant force 500 N.

In Fig. 1a,b are shown the curves of strain as a function of time, in days, over a period of 30 days, for 500 mm long glulam beams bonded with the best, standard-approved polyurethane adhesive, after being subjected to a constant load of respectively 1500 N (Fig. 1a) and 500 N (Fig. 1b). These show when gluing at 11 % equilibrium wood moisture content (emc) and ambient temperature that the level of creep of a polyurethane bonded glulam beam is small, but in constant progress. While the results after 30 days under controlled humidity and temperature show a low level of creep, which is indeed comforting, the curves in Figs. 1a,b and more clearly in Fig. 1b show a constant regular progression of strain with time. The indications are that the beams in Fig. 1b continue to creep at the same strain rate, without having stabilized, at ambient temperature, after 30 days, which is indeed worrying. The same trend is noticeable in Fig. 1a; although the progression is not as regular as what shown in Fig. 1b.

Tab. 1: Shear strength and percentage wood failure results of laboratory glulam beams bonded with the best, european approved, polyurethane structural adhesive, when bonding at 50, 30 and 15 % wood moisture content.

Wood moisture content	50 %		30 %		15 %	
	Shear strength (MPa)	Wood failure (%)	Shear strength (MPa)	Wood failure (%)	Shear strength (MPa)	Wood failure (%)
Dry						
- 2 h after prepar.	3.32	0.0	4.06	0.0	9.01	97
- 4 h after prepar.	2.40	0.0	2.63	0.0	9.17	100
- 24 h after prepar.	2.25 ¹	0.0	2.86 ³	0.0	8.12 ⁵	67
- 7 days after prepar.	2.73 ²	0.0	3.70 ⁴	0.0	7.38 ⁶	50
24 hours cold soak						
- 24 h after prepar.	1.94 ¹	0.0	2.06 ³	0.0	3.05 ⁵	33
- 7 days after prepar.	2.34 ²	0.0	3.22 ⁴	0.0	4.39 ⁶	0.0
2 hours boil						
- 24 h after prepar.	2.38 ¹	0.0	2.49 ³	0.0	7.42 ⁵	43
- 7 days after prepar.	1.86 ²	0.0	2.44 ⁴	0.0	3.97 ⁶	0.0

¹ emc decreased from 50 to 47.7 %

² emc decreased from 50 to 44.1 %

³ emc decreased from 30 to 26.3 %

⁴ emc decreased from 30 to 22.4 %

⁵ emc decreased from 15 to 12.2 %

⁶ emc decreased from 15 to 10.7 %

The equilibrium moisture content (emc) of the wood during bonding and at which the glulam beams are maintained has also an important effect on the performance of polyurethane-bonded glue-lines. In Tab. 1 are reported the shear strength results and percentage wood failures at 15, 30 and 50 % wood emc of glueing at different periods after beech joint preparation. The initial strength results for the specimens when dry are reported as well as the results after 24 hours cold water soaking and after 2 hours boiling. The results show that the higher is the wood moisture content of the wood at gluing, the lower are the strength results obtained on testing at that moisture content. This is expected, and all the results reported in Tab. 1 increase

as one passes from 50 to 30 and 15 % wood moisture content at gluing. As the sample slightly dries the strength improves in the great majority of cases. These trends are valid for both dry specimens and specimens having undertaken 24 hours cold water soaking and 2 hours boiling. General trends are also, as expected, that at all equal times after preparation, the strength results after 24 hours cold soaking are lower than the dry results. The strength results after 2 hours boil are lower than the dry results and higher than the cold soak ones for the specimens tested 24 hours after joint preparation. This is expected as after 24 hours the bondlines are obviously not completely cured and application of heat by undergoing the boil test further cures the specimens yielding better strength. This trend is inverted, as it could be expected, when testing specimens aged of 7 days. In this latter case the strength results after 2 hours boil are lower than the cold soak ones because the bondline has been fully cured and only heat degradation occurs.

All this means that in wet wood gluing, while bonding with polyurethanes does occur, this is (1) far from the requirements of any structural standards, and (2) the specimens need to be left to be redried to pass the requirements of relevant standards. Once redried, or when the wood is bonded dry, excellent results are obtained. Thus, the advantages of wet wood gluing with polyurethanes are subject to the considerable disadvantage of redrying that applies to any other type of wet wood gluing adhesives (Properzi et al. 2002).

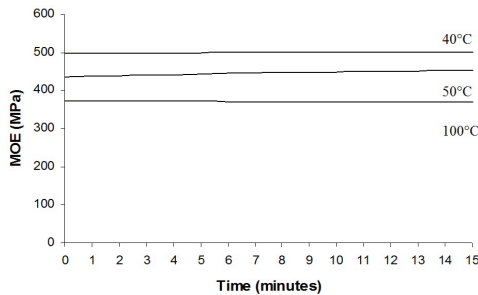


Fig. 2: MOE as a function of time and temperature in 40, 50 and 100°C isothermal thermomechanical analysis in bending of cured beech wood joints bonded with best commercial one-component polyurethane adhesive for structural wet and green wood gluing.

As regards temperature dependent creep, its extent for the best standard approved polyurethane is shown on Fig. 2 where isothermal thermomechanical analysis (TMA) was done for bonded beech joints. The polyurethane under examination clearly presents temperature dependent creep as shown by the considerable decrease in proportion of the MOE of the joint as the temperature increases. While this decrease is lower than that observed for the other two polyurethanes approved for the same use in Europe (Na et al. 2005) it must also be remarked that the initial MOE imparted to bonded joints by this polyurethane is lower than that of the other two. A decrease of 16 strength and 22 % passing from 40 to respectively 50 and 100°C is noticeable in Fig. 2. It has already been shown that the lower the initial strength the lower the temperature dependent creep (Na et al. 2005). The temperature-dependent creep improvement noted in this test for the urethane under examination can perhaps be interpreted in this context. and the Comparison of this polyurethane. It has already been established that a higher level of reticulation can at least minimize this problem (Na et al. 2005). This urethane can then be improved, the remarks and conclusions reported here refring exclusively to the adhesife formulation as used at the moment of writing this article.

The ^{13}C NMR spectra of the best performing commercial polyurethane and its details are shown in Figs. 3a,b,c according to the shifts pattern already established and referred to (Na et al. 2005).

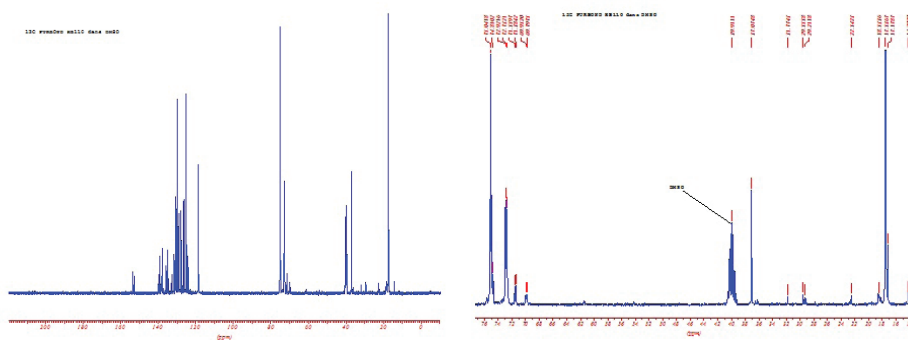


Fig. 3a

Fig. 3b

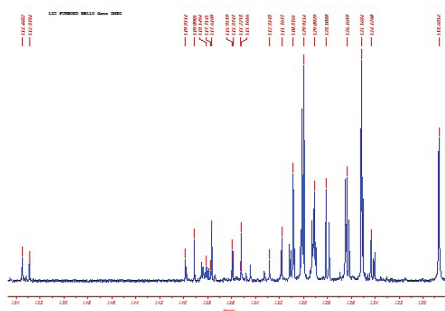
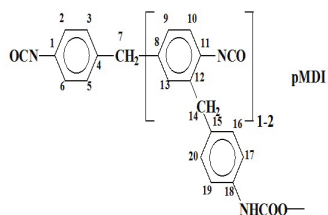


Fig. 3c

Fig. 3: ^{13}C NMR spectrum of a) best commercial one-component polyurethane adhesive approved by european standards for structural wet and green wood gluing, b) details of the 110–154 ppm region of the spectrum, c) details of the 14–76 ppm region of the spectrum.

The spectra show peaks for pMDI-derived and TDI-derived urethane residues, at 137–139 ppm (Ar C-CH₂- in *para* or in *meta* to a -NCO group), at 135.1–135.9 ppm (Ar C-CH₂- in *para* to a -NCO group), the peaks around 130–132 ppm (Ar C-NCO in *para* to a -CH₂- group), and at 118–119 ppm (here 118.6 ppm, Ar C *meta* to a -CH₂- and *ortho* to a -NCO group; as well as Ar C *ortho* to a -CH₂- (C17,19), and also *para* to a -NCO group). The C7,14 peak (-CH₂- of pMDI) that should be present at 40.7 ppm is masked by the broad pattern of the DMSO solvent used. Also visible are the other aromatic carbons of the pMDI cycle, namely 124.3 ppm (C2,6), 125.1 ppm (C10), 125.9 ppm (-N=C=O), 126.3 ppm (C9), 128.1 ppm (-N=C=O), 129.0–129.9 ppm (C13,16,20), 130.06 ppm (C3,5), 131.7–131.9 ppm (C1 and C18 when linked to an unreacted -N=C=O group), 132.5 ppm (C12), the 135.1–135.2 ppm representing the C15 linked to a bridge that by software calculation estimate¹⁷ should appear at 134.5–134.6 ppm, 135.8–135.9 (C1 and C18 when linked to a urethane bridge), 138.1 ppm (C4,8), and 158.3 and 153.5 ppm (the NHCOO- carbon of the urethane bridge).



Overimposed to the pMDI pattern and partly hidden by it there is a smaller TDI pattern at 17 - 18.6 ppm (Ar-CH₃), 130.8 ppm (aromatic C *ortho* to -CH₃ and *meta* to the two -NCO or urethanes), 139.0 ppm (aromatic C *para* to -CH₃ and linked to one -NCO or urethane, and *meta* to the second -NCO). The signal at 128.0 is that of the -NCO of the TDI next to one of the -NCO of the pMDI.

The pattern of the polyols or diamines used is relatively more complex. At 69 ppm and 71 ppm are present two of the carbons (-CH₂- and -CH-) of a polyoxypropylene from 1,2-propylene glycol, and at 17.1-18.6 ppm its -CH₃ group. The rest of the peaks of the polyols belong to free and etherified polyalcohols where considerable proportion of secondary alcohols or ether groups are present. Thus, for example, a polyalcohol such as sorbitol [HOH₂C(CHOH)₄CH₂OH] would present for the four secondary alcohol functions shifts of respectively 74.5, 72.9, 74.3, and 76.1 ppm, which fit within the +1 ppm precision of the spectra with the 72.7-72.9 and 74.8-75.1 ppm patterns observed experimentally.

CONCLUSIONS

The conclusions which can be drawn is that the best industrial one-component polyurethane adhesives for green and wet wood gluing, as the other studied previously, presents too temperature-dependent creep, this being one of their intrinsic characteristics. The encouraging result is that its ambient temperature creep is lower than others. However, attention should be paid to the constant, even-growth ambient temperature creep that does not settle to a MOE plateau even after 30 days of applying a constant force in three point bending experiments.

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